A Determination of the Heat of Vaporisation of Water at 100° C. and One Atmosphere Pressure in Terms of the Mean Calorie.

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A.—Introduction.

The value of the latent heat of vaporisation of water at 100° C. and one atmosphere pressure is here measured directly in terms of the mean calorie by using a steam calorimeter that may be regarded as a development of Joly's classical apparatus. It is claimed that a high degree of accuracy has been attained on account of—

(1) An ice-bath that remains steady for one or two hours;

(2) A shielding device, by means of which a damp body can be left hanging in a steam chamber without loss or gain in weight; and

(3) A determination of the effect of the dampness of the steam.

B.—Theory of the Method.

The temperature of a bulb of thermal capacity K is raised from the freezing point θ to the boiling point Θ by surrounding it with steam, a mass m of steam being condensed on the bulb, where

$$\mathrm{K}(\Theta-\theta) = m\mathrm{L}.$$

The bulb is then filled with water (of mass M) and the process repeated, a mass m' of steam being condensed, where, omitting small corrections,

$$(\mathrm{K}+\mathrm{M}s)(\Theta-\theta) = m'\mathrm{L},$$

whence

$$\mathrm{L} = \frac{\mathrm{M}s}{m'-m}(\Theta-\theta),$$

i.e., the heat of vaporisation is measurable in appropriate calories ($s = 1$) in terms of a temperature difference and the ratio of the masses M and $(m'-m)$.

C.—Apparatus.

C I. *Outline of Apparatus.*

The apparatus, as shown in the diagrams (figs. 1–3), consists of—

1. A balance, from one arm of which is suspended a windlass, W. This raises and lowers the bulb and pan, B, P. These may be raised into the

chamber 1, or lowered into the chilling vessel 2, or the steam bath 3, either of which may be attached directly beneath 1.

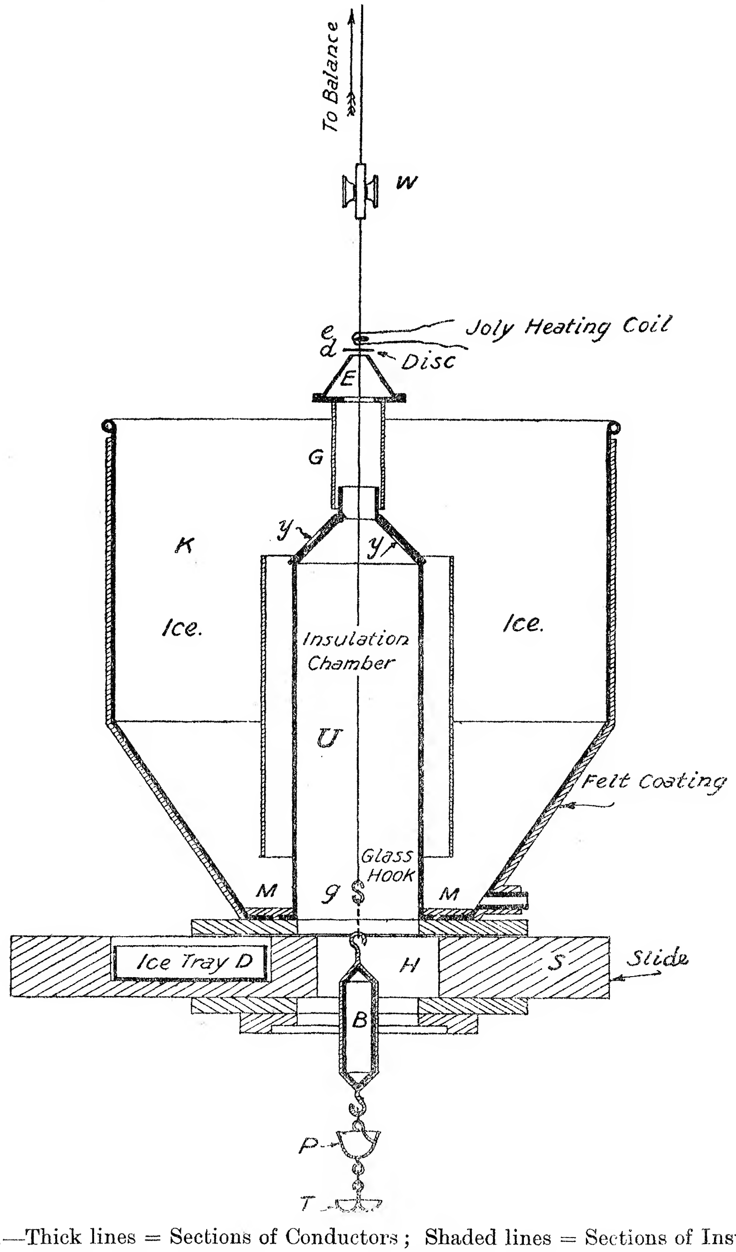

Fig. 1.—Thick lines = Sections of Conductors; Shaded lines = Sections of Insulators.

2. A cast brass vessel, 1, of the shape shown, surrounded by an insulating felt jacket. Attached to the bottom of the vessel are insulating blocks,

through which passes an insulating slide S, containing a depression D, and a circular hole H. The space K is filled with ice to the level of the glass tube G, and the slide is placed so that the depression D (containing a dish of ice) is brought directly below the inner chamber U of the vessel 1, and closes it. The walls, floor, and top of that chamber are then at 0° C., and a bulb enclosed therein, if initially at 0° C., will remain at that temperature indefinitely. When the slide is moved so that the circular hole H is directly

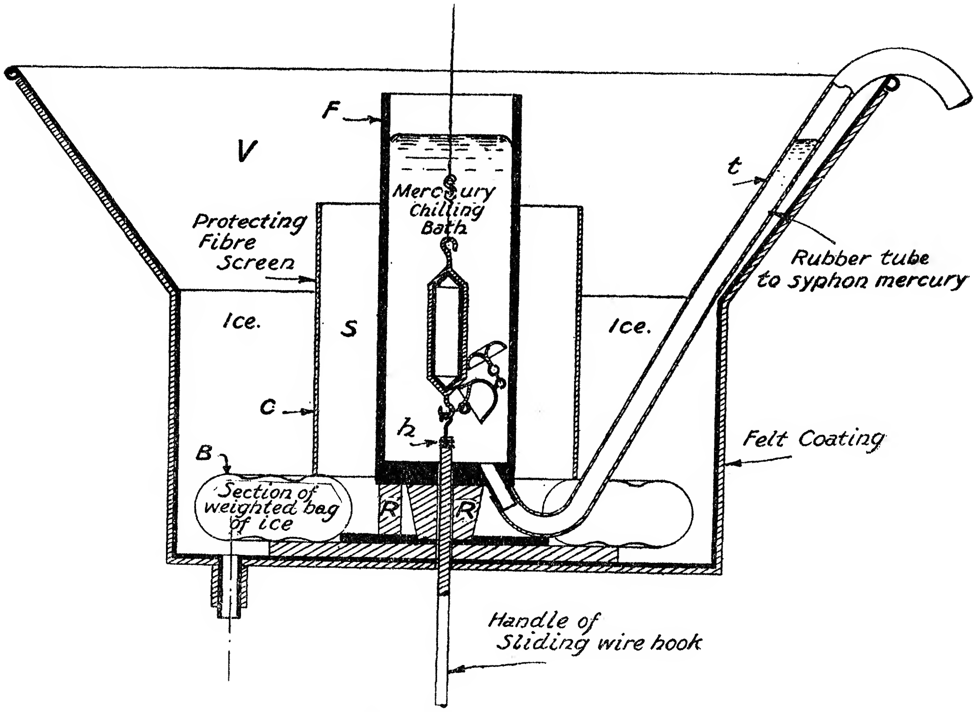

FIG. 2.—Chilling Vessel.

below the inner chamber U, the latter is placed in communication with the vessel attached below, which may be either the chilling chamber 2 or the steam chamber 3.

3. A chilling chamber 2, consisting of a hollow iron cylinder F, into which mercury can be run by means of a rubber tube, and an outer vessel V, which can be filled with a mixture of ice and water.

4. A steam jacket 3, described in C XIII.

5. A "tin" boiler with electrical attachments (C XII).

C II. *Outline of Process.*

In the early part of the experiment, the chilling chamber 2 is placed directly below, and in contact with, the inner chamber of 1, U. The weighed bulb is lowered into the iron chamber F by means of the windlass, and is attached to the bottom of the chamber by the hook *h*. Mercury is then run in by the rubber tube *t*, the outer vessels, V and K, are filled with ice and water in the manner described in C IX, and the whole allowed to cool for

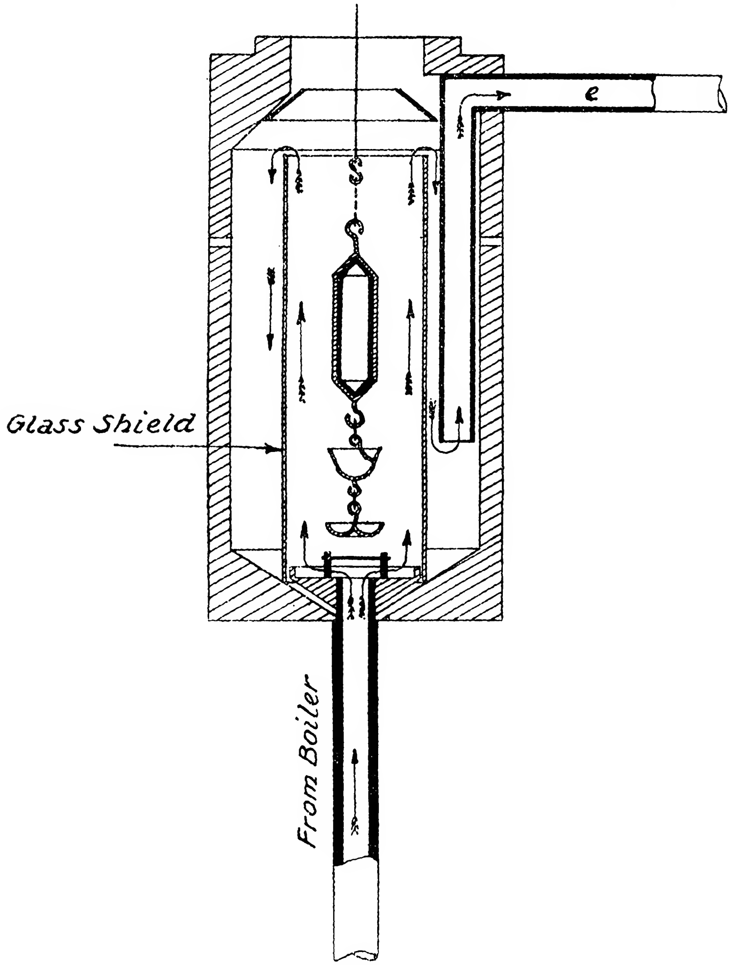

FIG. 3.—Steam Jacket.

one hour. The mercury is then syphoned off, the bulb released from *h*, and raised by the windlass into the inner chamber U of the vessel 1, and the slide so moved that the ice-filled depression D closes the upper chamber. The bulb is now in the insulated position described in C I (2); it is again

weighed, the ice mixture is removed from the chamber K; the chilling chamber 2 is removed, and its place taken by the steam chamber 3. The steam supply is then increased to the full; the cone C is moved so that the exit holes y, y, are free; simultaneously the outlet e (fig. 3) is blocked, and the slide is moved so that the upper chamber U is connected with the steam chamber 3 by means of the hole H. While the bulb and pan are being lowered into 3, the steam mounts into U, the supply is adjusted to the predetermined amount, the outlet e is freed, and the exit holes, y y, are closed. The consequent condensation is that due to the definite temperature change from the ice point to the boiling point under those particular conditions, and its amount may be determined by weighing the bulb in the manner described in C XIII, while it is still suspended in the steam.

C III. *The Bulb.*

The glass bulb of 8 to 10 c.c. capacity contains water and some platinum foil, so arranged that convection can take place freely. On account of the poor conductivity of the glass, the surface of the bulb rapidly approaches the temperature of the steam, and the water which condenses on its surface attains the boiling point before it reaches the glass pan P. Consequently, the condensation on the lower side of the pan itself is small (two drops), and is collected in the little glass tray T. This tray is constructed in the ◡◡ shape shown, so that the one large drop that collects on its lower surface can be held there securely.

C IV. *The Filling of the Bulb.*

The condensation m' is determined with the bulb nearly filled with water, the condensation m with a little water left in, so as to ensure that the interior is saturated with vapour at the higher temperature. Between these operations the bulb is opened by touching one of its fine convoluted ends on a grinding wheel, is filled with distilled water freshly boiled in a platinum vessel, and closed with a thin blow-pipe flame. By this means (1) the average temperature of the air within the tube at the time of sealing is known to within some five degrees; (2) the loss of glass is reduced to between one and three tenths of a milligramme—the thermal capacity of this lost glass is negligible, but these tenths of a milligramme must be obtained by weighing before and after the operation, and subtracted from the apparent weight of water added.

C V. *The Joly Coil and Disc.*

When the steam passes through the upper chamber 1, there is a tendency for condensation to take place at the narrow exit E. This has been prevented, as in the Joly experiment, by the electrically heated coil *e*, which encircles the suspension wire and warms the exit disc *d* by radiation. This disc has a small central hole, through which the suspension wire passes; it is light, and swings with the wire until the oscillations become smaller than the diameter of the hole; the disc then becomes steady, and the wire hangs freely through the small central hole.

C VI. *The Glass Hook.*

As the coil *e* is kept red, a little heat is conducted down the suspension wire (silver, about 50-gauge). The glass hook *g* has been inserted to check and control this quantity, which is really very small. The continuous outward flow through E carries upward and away any steam that may have come in contact with the upper portion of the suspension and become slightly superheated, and prevents any consequent evaporation from the bulb.

C VII. *The Chilling Vessel* (2).

To bring the glass bulb and its attachments to the ice-point, and subsequently remove it, with few or no particles adhering, it is necessary to surround it with a conducting liquid that does not wet glass. For this reason, the chilling vessel V contains an iron cylinder F (suitably insulated by the rubber and fibre packings R, R), into which mercury can be poured by means of the tube *t*.

The dimensions of the platinum connecting chains *c*, *c*, are arranged so that the wire hook *h* can hold the bulb and pans as shown in diagram (BPT), floating inverted in the heavy mercury.

C VIII. *Adherent Mercury and Water.*

Mercury is syphoned through the tube *t*, and surrounds the bulb with the required conducting material. During the chilling traces of water may be deposited on its surface. On syphoning off this mercury, releasing the bulb, raising it into U and closing that chamber with the slide S, the apparent weight of the bulb will be found to have increased. The increase is the mass of adherent particles of mercury and water. The mass of mercury is obtained by drying the bulb directly after the experiment, and weighing it before and after wiping off the fine globules of mercury. The mass of water

is then determined by difference. These masses need not be large, and corrections can be applied with considerable accuracy (see E V).

The alternative method of passing a stream of dried chilled air through the air-space, and so avoiding this deposition of dew, was found to vitiate the insulating properties of the upper chilling chamber U, as the temperature and humidity of the dried air could not readily be regulated.

C IX. *Circulation in the Chilling Vessel.*

To ensure that the mercury in the chilling vessel, and consequently the bulb, reaches the ice point, a slow circulation is caused in the surrounding jacket. The vessel in fig. 2 (while placed directly below and touching that of fig. 1) is filled with ice, some of which is kept at the bottom by the weighted annular net bag B. Pressed down on this is the hollow fibre cylinder C. When a steady state is reached, heat enters mainly at the side of the vessel—the slightly warmed water is the heavier and sinks, and the lighter ice-cold water within the fibre cylinder rises. The warmed water percolates slowly through the ice bag B on its way to the inner side of the cylinder C, and is thus chilled effectively so long as there is ice in B. The amount of ice in S is so chosen that it all melts in the initial stages of the cooling, and S becomes filled with ice-cold water continuously replenished by means of the circulation through B. Supercooling is thus avoided.

A similar arrangement is used with the insulation chamber (fig. 1).

In an actual experiment the chilling vessel is attached directly below the insulation chamber, and it will be seen that the mercury bath in F is surrounded by (1) the ice in V and S, (2) the chilled air of the insulation chamber, (3) the rubber R and wooden handle of the hook *h*, (4) the rubber of the tube *t*. Of the heat that leaks in, the greater portion comes through R, and an estimation of its order of magnitude may be of value.

In the figure the thickness of the steel vessel F has been exaggerated for the sake of clearness: its real thickness is about 1 mm. Seeing that the conductivity of the steel is some 250 times that of the rubber or the wood and the area of contact some 20 times greater, a temperature gradient in the steel 5,000 times smaller than that in the rubber would balance the said leak. Assuming a temperature difference of even 10° C. between the two ends of the rubber, it follows that the leak would maintain in the mercury a temperature only 0·0001° higher than it would otherwise have been. As an accuracy of 0·01° corresponds to an accuracy of one ten thousandth part of the temperature interval (100° C.), it is taken that if the mercury assumes a steady temperature at all during the experiment, that temperature is the ice point.

To check this, the chilling vessel 2 has been removed from the insulating chamber 1, and set up separately; a Beckmann thermometer inserted in the mercury in F, and the mouth of F loosely packed with cotton wool. The tendency for leaks of heat is much greater in this case, but the constancy of the temperature attained is clearly shown. Two sets of readings are given, as typical of a dozen such experiments. For the sake of comparison one set of readings is given for an experiment in which the fibre cylinder has been removed.

The magnitude of these Beckmann degrees is approximately that of a Centigrade degree. The Beckmann zero has no direct relation to the ice-point.

Table I.

Time.	Beckmann Readings.		Time.	Beckmann Readings.	
	Experiments with Fibre Cylinder.				
p.m.			p.m.		
3.25	Insert		3.50	Insert	
3.30	3·08°		3.55	3·060°	
3.35	3·06°		4.10	3·040°	
3.40	3·048°		4.23	3·030°	
3.41	3·047°		4.28	3·021°	
3.46	3·046°		4.30	3·021°	
3.49	3·046°	Steady period 1 hour.	4.35	3·021°	
4.12	3·048°		4.50	3·021°	Steady period 2 hours 44 mins.
4.19	3·049°		5.15	3·020°	
4.30	3·048°		5.27	3·020°	
4.35*	3·047° *		5.50	3·020°	
4.46	3·053°		6.35	3·020°	
4.56	3·059°		7.12	3·021°	
5.4	3·056°		7.30	3·032°	
5.27	3·075°		8.5	3·060°	
5.37	3·091°		9.22	3·123°	
5.42	3·080°		9.50	3·173°	
5.50	3·089°		11.20	3·661°	
7.2	3·149°				
	Experiments without Fibre Cylinder.				
a.m.			p.m.		
11.30	Insert		12.43	3·062°	
11.39	3·17°		12.48	3·063°	
11.52	3·07°		1.19	3·080°	
11.56	3·060°		1.24	3·22°	
p.m.			Stir thoroughly		
12.6	3·056°		1.25	3·08°	
12.22	3·056°		1.26	3·060°	
12.35	3·052°				

* Temperature of water outside fibre cylinder is now 1·5° C.

C X. *The Manipulation of the Insulation Chamber.*

The upper chamber U is used, firstly as part of the chilling chamber,* then, on closing the slot, as an insulation chamber in which the chilled bulb remains at the ice point, and, subsequently, on again opening the slot, as part of the steam chamber.

During the first stage the slot is open, and the bulb lies in the lower chilling chamber. The space K is filled with ice bags, placed round a fibre cylinder in a manner similar to that described in C IX.

During the second stage, the bulb is raised and the slot shut, giving the condition of insulation described in C I. The bulb remains here while the lower chilling chamber is being replaced by the steam chamber. When this is attached, and before the slot is opened again, *i.e.* while the ice in the tray D is still slowly melting, the ice bags in K are removed, the water run off, and the watertight conical cover, *yy*, rotated so that its three large circular holes come opposite the three large circular holes in the top of the chamber U. The slot is then opened, the Joly coil switched on, and the bulb lowered rapidly into the steam chamber. As the slot is being opened, the exit *e* of the steam chamber is corked, so that the steam can be made to rush into the upper chamber; subsequently *e* is opened, *yy* closed, and the flow of steam regulated to the pre-arranged amount.

As the steam rushes into the cold chamber U, driving the air before it, a belt of fog is formed at the surface of contact of the cold air and steam. This belt is set whirling and rapidly ejected, some portion of it becoming attached to the sides of the vessel and to the bulb. This is the most serious difficulty that has been encountered, and probably determines the limit of accuracy of the method. (For discussion, see E VIII, Accuracy.)

In this third stage, a stream of water is continually trickling down the sides of the chamber U, and though its magnitude is lessened by covering K with a wooden lid, great care must be taken to conduct the stream smoothly over the junction of the upper and lower chambers in order to prevent splashing.

C XI. *The Slide and Slot.*

After considerable experimenting, it was found that a suitable slide and slot could be made out of a block of pine wood, dried for some 70 hours, and subsequently enamelled, a steam-tight fit being secured by covering the sides with strips of soft stretched felt. The difficulties are due to the facts that

* Care is taken that the insulation vessel U is surrounded with either freezing material or poor thermal conductors. For this reason, the annular crack MM has been made in the continuity of the metal vessel.

the slide is subjected to considerable temperature gradients, is exposed to steam, and moves in a slot that expands as the temperature rises. The slot must be dried carefully after each experiment, and frequently scraped, baked, and re-enamelled.

C XII. *The Production of the Steam.*

The steam is generated electrically, a bare eureka wire immersed in water being heated by an alternating current of 40 volts and about 8 amperes.

The advantages of this method are :—

(1) Quick response due to the small thermal capacity of the wire—the steam flow changes immediately the current is altered.

(2) Accurate adjustment of flow—a change in the electric current produces a proportionately smaller change in the upward pressure due to the steam flow. This permits of very accurate reproduction of the steam flow, the importance of which lies in the fact that, when this pressure can be reproduced, its magnitude is of no importance in determining the difference $m'-m$ of the two weighings in the steam chamber.

(3) The surface of the vessel cannot rise in temperature above the boiling point, as its only source of heat is the steam and water within.

(4) There is no electrolysis, as the current is alternating.

(5) By shielding the boiler and exit tubes from draughts, the degree of dampness of the steam seems to have been controlled (E VII), and its actual value seems to have been small (E IX).

C XIII. *The Steam Chamber and Radiator Correction.*

The steam chamber used by Joly was a double-walled copper vessel, the inner surfaces of which were "clean but not bright." By this means he found that a body immersed in the steam increased in weight after the initial condensation at the rate of "1 milligramme in 10 minutes." It has been found that a silvered vacuum flask reduced this to 1 milligramme in 20 minutes. The increase is due to radiation through the steam from the body at boiling point to the inner surface of the copper slightly below boiling point. It seemed, therefore, that the radiation would be checked by a glass cylinder placed as indicated in diagram 3. The outer surface of the glass will tend to become slightly chilled by radiation to the inner surface of the copper. This tendency will be counteracted by an immediate condensation of steam on the slightly chilled surface, and as the glass is a good insulator, no appreciable amount of heat can leak from the inner to the outer surface of the glass, especially as the temperature gradient is so small. Consequently the inner surface of the glass is kept very exactly at the temperature of

boiling, and loss of heat to it from the bulb is inhibited. A body immersed in a steam jacket of this kind will retain a steady weight for periods as long as 20 or 40 minutes, as is shown by the figures of Table II. Such steady readings during this long period of balance (see E VII) enable values to be obtained for m and m' under corresponding conditions without any time correction, and with the balance-arm swinging under just those steady conditions that are favourable to the accurate determination of a weight.

Table II.

Time.	—	Time.	—
3.2.15—		4.2.15—	
11.56 a.m.	Bulb lowered	1.4 p.m.	Bulb lowered
12.0 noon	29·290 grm.	1.10 ,,	35 237 grm.
12.2.0 p.m.	29·2909 ,,	1.15 ,,	35·2384 ,,
12.3.30 ,,	29·2913 ,,	1.18 ,,	35·2389 ,,
12.5.0 ,,	99·2918 ,,	1.20 ,,	35·2387 ,,
12.6.20 ,,	29·2917 ,,	1.25 ,,	35·2388 ,,
12.7.30 ,,	29·2917 ,,	1.29 ,,	35·2389 ,,
12.8.30 ,,	29·2918 ,,		
12.11.0 ,,	29·2916 ,,	23.2.15—	
12.16.30 ,,	29·2918 ,,	2.12 p.m.	Bulb lowered
12.20.0 ,,	29·2916 ,,	2.17 ,,	29·8890 grm.
12.25.0 ,,	29·2918 ,,	2.20 ,,	29·8920 ,,
12.27.0 ,,	29·2923 ,,	2.23 ,,	29·8932 ,,
12.30.0 ,,	29·2901 ,,	2.25 ,,	29·8932 ,,
12.31.0 ,,	29·2887 ,,	2.30 ,,	29·8932 ,,
		2.35 ,,	29·8933 ,,
10.7.15—		2.40 ,,	29·8951 ,,
2.36 p.m.	Bulb lowered	2.43 ,,	29·8921 ,,
2.44 ,,	28·4000 grm.	2.45 ,,	29·8894 ,,
2.46 ,,	28·4004 ,,		
2.49 ,,	28·4002 ,,	31.7.15—	
2.51 ,,	28·4003 ,,	5.52 p.m.	Bulb lowered
2.55 ,,	28·4003 ,,	6.0 ,,	33 79 grm. (approx.)
2.56 ,,	28·4000 ,,	6.6 ,,	33·7890 grm.
2.58 ,,	28·4002 ,,	6.9 ,,	33·7915 ,,
2.59 ,,	28·4002 ,,	6.11 ,,	33·7913 ,,
3.1 ,,	22·4001 ,,	6.13 ,,	33·7915 ,,
		6.15 ,,	33·7915 ,,
		6.22 ,,	33·7916 ,,

D.—*Corrections to be Applied.*

(I) Corrections due to changes occurring within the bulb. These changes consist of change of temperature, evaporation of sufficient liquid to saturate the enclosed space with vapour, and change of pressure.

Apart from the negligible expansion of the bulb, no external work is done. The heat entering the bulb is therefore equal to the change in internal energy $\int dU$. This quantity depends on the initial and final states of the substances and is independent of all intermediate states. The quantity of heat entering can therefore be obtained as follows:—

The complete expression for the change of internal energy may be written in the customary notation

$$\int dU = \int C_v dT + \int T^2 \frac{\partial}{\partial T}\left(\frac{p}{T}\right)_v dv,$$

per unit of mass.

The terms $\int T^2 \frac{\partial}{\partial T}\left(\frac{p}{T}\right)_v dv$ which may have to be dealt with here are small. The largest is that which refers to the compression of some 4 c.c. of water vapour from 1 atmosphere to $2\frac{1}{3}$ atmospheres, approximately, at a temperature of 100° C. Its value may be found by taking

$$(v-b) = RT/p + c/T^n$$

as the characteristic equation of the vapour.

Whence

$$\frac{RT^2}{p^2}\frac{\partial}{\partial T}\left(\frac{p}{T}\right)_v = -nc/T^{n+1} = -n\{(v-b)p-RT\}/Tp,$$

therefore,

$$T^2 \frac{\partial}{\partial T}\left(\frac{p}{T}\right)_v = -np\{(v-b)p-RT\}/RT = \frac{na(v-b)}{v^3}$$

approximately, where a is a van der Waal's constant.

$\int_{p=1\text{ Atmos.}}^{p=2\frac{1}{2}\text{ Atmos.}} T^2 \frac{\partial}{\partial T}\left(\frac{p}{T}\right)_v dv$ is therefore of the order of na/v ergs per gramme molecule of vapour. This amount is insignificant.

The change of internal energy is therefore given to the required degree of accuracy as

$$\int dU = \int C_v dT.$$

To obtain the corrections due to changes taking place within the bulb, consider :—

(*a*) M grammes of liquid and μ grammes of air heated separately

$$\int dU = M \underset{\text{liquid}}{\int_{0^\circ C.}^{100^\circ C.} C_p dT} - M \underset{\text{liquid}}{\int_{0^\circ C.}^{100^\circ C.} pdv} + \mu \underset{\text{air}}{\int_{0^\circ C.}^{100^\circ C.} C_p dT} - \mu \underset{\text{air}}{\int_{0^\circ C.}^{100^\circ C.} pdv}.$$

(*b*) An amount of vapour $M_{\text{vap.}}$ evaporated separately at 100° C.,

$$\int dU = M_{\text{vap.}} L_I = M_{\text{vap.}} \{L_p - p(v_{\text{vap.}} - v_{\text{liq.}})_{100^\circ C.}\},$$

where L_I is the internal latent heat and L_p the latent heat (with 1 atmosphere pressure) at 100° C.

(The change of vapour-pressure with the absolute superincumbent pressure is of the order of 10^{-3} of this amount and negligible here.)

(*c*) The pressure of each changed to p' ($2\frac{1}{3}$ atmospheres approx.), all brought together and allowed to mix. To the order of accuracy required

$$\int d\mathrm{U} = 0.$$

The expression for the heat absorbed by the bulb $\int d\mathrm{U}$ is, therefore, the sum of the expressions on the right-hand sides of the above equations. In the case of the emptied bulb it is equal to $m\mathrm{L}_p$, and in that of the filled bulb to $m'\mathrm{L}_p$. Hence,

$$(m'-m)\,\mathrm{L}_p = \delta\mathrm{M}\underset{\text{liquid}}{\int_{0^\circ\,\mathrm{C.}}^{100^\circ\,\mathrm{C.}}}\mathrm{C}_p d\mathrm{T} - \delta\mathrm{M}\underset{\text{liquid}}{\int_{0^\circ\,\mathrm{C.}}^{100^\circ\,\mathrm{C.}}} p\,dv - \delta\mu\underset{\text{air}}{\int_{0^\circ\,\mathrm{C.}}^{100^\circ\,\mathrm{C.}}}\mathrm{C}_p d\mathrm{T} + \delta\mu\underset{\text{air}}{\int_{0^\circ\,\mathrm{C.}}^{100^\circ\,\mathrm{C.}}} p\,dv$$

$$-\,\delta\mathrm{M}_{\text{vap.}}\,\mathrm{L}_p + \delta\mathrm{M}_{\text{vap.}}\,p\,(v_{\text{vap.}} - v_{\text{liq.}})_{100^\circ\,\mathrm{C.}},$$

where $\delta\mathrm{M}$, $\delta\mu$, and $\delta\mathrm{M}_{\text{vap.}}$ are all positive.

The magnitudes of the terms on the right are approximately 400, 0·004, 0·10, 0·03, 1·30, 0·12 calories respectively. Since the experimental results cannot possibly give an accuracy greater than 1 or 2 parts in 10,000, the second and probably the fourth term may be neglected.

(II) A correction on the weight of water added to the bulb, due to the weight of air displaced by the added water. The weight of air displaced is about 1/1000th part of the weight of water added. An error of as much as 10° C. in the estimated temperature of the air in the bulb, at the moment of closing, would produce a consequent error no greater than 1 in 30,000 in the corrected weight of the water added.

(III) A correction for the buoyancy of the condensed liquid. The measured difference $(m'-m)$ must be increased by an amount equal to the mass of vapour displaced by the condensation excess in the case of the filled bulb.

(IV) A correction for the condensation due to the thermal capacity of the globules of mercury that may adhere to the bulb after the mercury has been withdrawn from the chilling chamber. These are recovered at the end of each experiment, and weighed. (C VIII and E V.)

(V) A similar correction for the condensation, due to any traces of moisture that may become attached to the bulb while it is in the chilling chamber. (C VIII and E V.)

(VI) A correction for the change of latent heat with temperature. The boiling point has varied from 100·27° C. to 99·41° C., corresponding to a variation of some 1 in 1000 in the supposed values of the latent heat. The consequent change in the condensation is of the order of 0·2 or 0·3 mgrm., and is corrected with sufficient accuracy by subtracting (or adding) directly from the condensation.

It will be seen that the above corrections are capable of being definitely determined. Any doubt as to their magnitude does not exceed 0·03 mgrm., though the size of the correction may be as large as 2 or 3 mgrm.

(VII) Corrections for convection, due to the heated parts, upward kinetic pressure of the stream of steam, buoyancy of the bulb (apart from the water condensed), and so on, although serious obstacles to the determination of the individual weight, are of minor importance in the present case. For this particular purpose, the difference of the weights m' and m is required. The special forms of electric heater and radiation screen (C XII and C XIII) have been devised with a view to keeping these disturbing influences of the same magnitude in both sets of weighings, so that their effects cancel when the difference $(m'-m)$ is taken. The constancy with which these conditions are maintained is discussed in E VII.

E.—Limits of Accuracy.

E I. *The Temperature Interval.*

It has been shown (C XIII) that the weight difference $m'-m$ can be determined to about one or two parts in 10,000, *i.e.*, 0·1 mgrm. It is sufficient, therefore, to measure the temperature interval (about 100° C.) to the nearest 0·01° C.

(*a*) The temperature of the steam is determined by reading the barometer and correcting for the difference of level between it and the steam chamber. To ensure that the pressure within the chamber is not appreciably greater than that outside, the size of the exit tube has been increased, so that when boiling begins no change can be observed in the level of the water in the bent glass tube fitted into the side of the boiler. Consequently, it is taken that the temperature is measurable to within about 0·005° C.

(*b*) As has been described previously, the bulb is brought to the ice point by surrounding it for upwards of an hour with mercury in a steel cylinder, the outside of which is surrounded with water, kept at the ice point by means of a free and continuous circulation through a region of melting ice. As the ice does not come into direct contact with the metal, the temperature attained by the bulb cannot fall below that of the water. This avoids super-cooling of the bulb and the formation of ice within the bulb. The effect of possible heat leaks has been already discussed. The actual temperature of the melting point is obtained by analysis of the water at the conclusion of each experiment (estimation of total solids, and of carbonate present). If these impurities approached a concentration sufficient to alter the melting point $\frac{1}{500}$° C., the results of the experiments were ignored. It may be

pointed out that a supercooling of even $\frac{1}{500}^\circ$ C. could by its cumulative effect freeze some of the pure water in the bulb, but an estimate of the amount of heat passing from the bulb when this very slight gradient is attained shows that this amount is immeasurably small.

It is argued, therefore, that the temperature interval has been measured to the 0·01° C. required.

E II. *The Use of the Balance.*

Manly* has determined the precautions that must be taken in the accurate use of a balance. Screens have been used in accordance with his directions and an attempt has been made to measure the temperature coefficient of the balance. This was found, however, to be quite small for the instrument used, and for the temperatures of experiment did not affect the weight by 0·1 mgrm.—the accuracy aimed at.

E III. *The Weights.*

The expression for the latent heat involves only the ratio of certain weights, *i.e.* $(m'-m) : \mathrm{M}$. It is sufficient, therefore, to calibrate the weights carefully against one another. This has been done before and after the experiments, and between the two series of experiments.

E IV. *The Weighing in Air—Degree of Dryness.*

(*a*) *Before Chilling.*—As the bulb is of glass, it collects on its surface a thin film of moisture. It is necessary that this film should be constant rather than absent. A number of weighings, taken under varied conditions as opportunity offered, showed that the weight of water expelled, on heating the bulb in a steam oven for a quarter of an hour, did not vary to any considerable extent (0·0002 grm.) with the humidity of the air which has previously surrounded it. On this account, it was found best to dry the bulb in a desiccator, and then to leave it hanging in the air for about an hour before weighing. By that time a steady weight is attained, and the mass of attached moisture is believed to vary from experiment to experiment by less than 0·25 mgrm., an amount which produces a change of 0·05 mgrm. in the mass of water condensed subsequently.

This has been found true of a room in Melbourne facing north, and for the degree of humidity usually experienced there during winter. It would seem that it is not true if the vapour pressure is low, *e.g.*, in a desiccator, or if the relative humidity is high.

(*b*) *After Chilling.*—When the bulb has been chilled in the mercury bath

* 'Phil. Trans.,' 1907.

and raised into the chilled insulation chamber, some few particles of mercury and a little moisture adhere to it. It is important that the weight in this chamber should remain steady, *i.e.*, there should be neither deposition nor evaporation of moisture. In the earlier trial experiments a current of cold dry air was passed to check the formation of water globules on the surface of the chilled mercury. It was found, however, that this caused evaporation when the bulb was brought out of the mercury bath. Attempts to dry the air-current to the required extent only, gave better results, but the best and steadiest results were found to be given by having no current of air at all, permitting a deposit of water globules on the mercury surface, and relying on the chilling of the upper insulation chamber to reduce the vapour pressure of the air it contains to the required amount 4·58 mm. It was found that this gave weighings steady to 0·1 mgrm.

E V. *Masses of Mercury and Water adhering to the Bulb.*

The difference between the weights before and after chilling gives the sum of the weights of mercury and of water. The weight of mercury alone is obtained by drying the bulb in a steam bath after the experiment and weighing before and after removing the particles of mercury. The weight of water is then obtained by difference.

Each of these adherent masses increases the condensation. On applying corrections for these, values of the mean specific heats of water and of mercury are required, and also of the heat of vaporisation of water. The sum of these corrections may amount to as much as 10 mgrm.; but the effect of an error of one unit in the value taken for the heat of vaporisation (539 say) will cause a consequent error as low as 0·02 mgrm., and an error of one-half of 1 per cent. in the value taken for the mean specific heat of mercury effects an error of about 0·01 mgrm. in the weighing—amounts which affect the result of these experiments by only 1 part in 30,000.

E VI. *Mass of Water Added to the Bulb.*

The water was prepared by distillation and subsequent boiling in a platinum vessel. The bulb and attachments were dried in a desiccator before weighing, and rapidly moved to a balance, the case of which contains a vessel of calcium chloride. The weight of water added is as much as 4 grm., so that an error of one or even two tenths of a milligramme is unimportant. In this determination, the weights of air displaced by the added water must be allowed for; knowledge of the temperature to within 20° C. is sufficient.

On enclosing boiled water with a sample of air, some solution necessarily

takes place. There is not sufficient carbon dioxide present to approach saturation of the water, so that none of this gas can be boiled off at the higher temperature. The effect of the solution in the water of oxygen, nitrogen, alkalies, etc., is more complex, but of too small an amount to affect the present work.

The method of filling the bulb is discussed in C IV.

E VII. *Determination of the Difference between the Masses of the Condensations.*

The apparent weight of the bulb and its attachments in the steam-chamber is affected by the convection upward due to the Joly coil, the upward pressure of the steam, the buoyancy of the steam, and so on. For the present purpose a difference of weights $(m'-m)$ is required, and consequently these disturbing influences are to be made constant rather than eliminated.

(*a*) The Joly coil heats the windlass and is itself hot. The variation in the effect of the consequent convective currents when the Joly heating current is increased by 1 ampère, is found to be 1·8 mgrm. As the heating current is adjustable to 0·02 ampère the convection currents can probably be reproduced without variation in the weight of more than some 0·03 mgrm.

In a similar way, the effect of changing the heating current in the boiler showed that the upper pressure of the steam was reproducible to 0·05 mgrm.; and violently fanning the boiler (without removing any screens) did not change the apparent weight by more than 0·6 mgrm.

It is taken, therefore, that under good experimental conditions these disturbances do not affect the apparent weight by the smallest detectable amount (0·1 mgrm.).

(*b*) The steadiness of the readings obtained when the bulb is in the steam chamber has been shown (C XIII) to allow of the determination of the apparent weight to 0·1 mgrm. This steadiness might be affected by dampness of the steam, radiation to sides of vessel, and conduction of heat down the suspension wire with consequent ebullition of the water condensed above the glass hook. It is not to be expected that the ideal conditions of absolutely dry steam (E IX), complete absence of radiation, etc., have been secured, although the effects of these have been lessened wherever possible. But it is claimed that the instrument has been so adjusted that these effects completely counteract one another for a very considerable period (a quarter or half an hour); and that the weighings are taken under those conditions of steady swing which are favourable to the accurate determination of a weight.

Presumably this balance is ultimately disturbed by the complete evaporation of the moisture above the glass hook, as the apparent weight always

increases before the ultimate rapid decrease begins which is due to the exposure of the heating wire as the level of the water in the boiler becomes low.

(*c*) The difference between the apparent weights (with filled and with emptied bulb) so obtained is the required difference $(m'-m)$ of the condensations less the weight of steam displaced by the excess of condensed water. This buoyancy correction can be applied with great accuracy.

It would seem, therefore, that each weighing should be correct to within 0·1 mgrm., and consequently the error in the difference $(m'-m)$ between any pair of weighings should not exceed 0·2 mgrm. That this is so, and that what may be called accidental errors are not great, is shown by the tabulated results of the two series of experiments, where the divergence of any one weighing from the mean is never more than two or three tenths of a milligramme. Consequently, the mean itself may be taken as correct to 0·1 mgrm.

A considerable number of experiments yielded results which indicated that a drop had fallen on to or off the bulb. As such a drop must weigh at least 30–50 mgrm., such results are readily isolated from the closely agreeing successful experiments, and have been discarded.

E VIII. *Condensation (Fog) in Insulation Chamber.*

A fog is formed when the steam from the steam jacket 3 comes into contact with the cold air of the insulation chamber. Some of this fog will become attached to the bulb. If the whole of the air in the chamber were to be mixed with steam, some 12 mgrm. would be condensed. The greater part of the air, however, is driven before the steam, and is expelled at the top of the chamber. As a liberal estimate of the amount of air mixing with the steam 10 per cent. can be taken, corresponding to a condensation of 1·2 mgrm. Most of this is ejected through the large holes at the top, and of that which remains the greater part will deposit on the walls of the chamber (which have a surface seven times that of the bulb). Consequently the fog deposited on the bulb itself does not exceed two or three tenths of a milligramme, and as it is merely the variation of this from experiment to experiment that affects the value of $(m'-m)$, no appreciable error will be introduced by this formation of fog.

E IX. *Dryness of the Steam.*

As has been pointed out in C XIII the weighings m and m' remain constant for a very considerable time and their constancy is not affected by traces of

liquid damp that may be carried bodily in the steam. It is certain, however, that every particle of damp in the litre or so of steam condensed will add unduly to the weight $(m'-m)$.

For this reason Callendar has preferred to neglect the values obtained by direct experiment, and adopts a higher value derived from the total heat formula and the specific heat of steam.

The question of dampness has been investigated in considerable detail by Richards and Mathews,* and by the author, who believes that its effect has been reduced to insignificant proportions.

Various precautions have been taken, such as (1) slow boiling, (2) wide tubes, (3) no traps, (4) screens and jackets to avoid draughts, (5) the radius of the rubber connecting tube about the size that gives maximum lagging,† etc., so as to reduce the degree of dampness. To actually test the effect of the damp remaining, it was intended to measure the apparent latent heats under different conditions of steam supply, and from these obtain an extrapolated value for dry steam. In the second series the electric current in the boiler was adjusted so that the steam flow was some 50 per cent. greater than in the first series—the steam was given off in a much larger number of smaller bubbles—and consequently it was considered that the degree of dampness, if at all appreciable, would have been considerably affected. Somewhat unexpectedly, the values obtained (538·86 and 538·89 mean calories) were found to be identical within the limits of accuracy of the weighings.

This agreement to within three units in the fifth figure is, of course, fortuitous. Each value, however, is the result of a number of separate measurements which are consistent among themselves; each may be expected to give, and has been found to give (see Tables), a value of the apparent latent heat correct to some one part in 7000.

It has been concluded on this account that the fourth figure above is correct in each case, and consequently that the dampness of the steam has not affected the fourth figure of the result. Hence, the value of the latent heat of dry steam has been taken as 538·88 mean calories.

* 'Proc. Am. Acad.,' 1911.

† Porter, 'Phil. Mag.,' 1906.

First Series. (Weighings are made to the fourth decimal figure. The fifth is introduced in the calibration corrections.)

—	Bulb nearly empty (six experiments).						Bulb nearly full (four experiments).			
	grm.	grm.	grm.	grm.	grm.	grm.	grm.	grm.	grm.	grm.
Weight (corrected) of bulb, etc., in air ...	27·88989	27·89120	27·89050	27·95542	27·95476	27·95596	31·78427	37·78408	31·78825	31·76626
Weight after chilling, etc.	28·02823	31·83042	29·54932	28·19326	28·97208	28·14806	31·96651	31·90090	32·71030	32·09985
Weight adhering mercury (recovered) ...	0·1172	3·9248	1·6222	0·2085	0·9918	0·1930	0·0000	0·1045	0·9174	0·3040
Weight adhering water	0·02114	0·01442	0·03662	0·02934	0·02552	0·00010	0·18224	0·11682	0·93205	0·33359
Sum of corrections for adhering mercury and adhering water	0·00463	0·02666	0·01669	0·00669	0·01082	0·00121	0·03383	0·00292	0·00837	0·00736
Weight of bulb, etc., in steam after condensation	28 39912	32·22232	29·93081	28·56256	29·34781	28·51562	32·07702	32·97785	33·79168	33·17803
∴ Apparent weight of steam condensed ...	0 37089	0·39190	0·38149	0·36930	0·37573	0·36756	1·11051	1·07695	1·08138	1·07818
∴ Corrected weight of steam condensed ...	0·36626	0·36524	0·36480	0·36261	0·36491	0·36635	1·07668	1·07403	1·07301	1·07082
	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.
Boiling point	100·27	100·09	99·93	99·41	100·00	100·32	100·20	100·01	99·87	99·69
	grm.	grm.	grm.	grm.	grm.	grm.	grm.	grm.	grm.	grm.
Hence, apparent weight of condensation per 100° C. temperature interval	0·36529	0·36494	0·36504	0·36476	0·36491	0·36517	1·07453	1·07393	1·07432	1·07392
Correction for change in latent heat with temperature of boiling	0·00010	0·00003	0·00003	0·00024	0·00000	0·00013	0·00024	0·00001	0·00016	0·00037
Hence, corrected apparent weight of condensation per 100° C. temperature interval	**0·36519**	**0·36491**	**0·36507**	**0·36500**	**0·36491**	**0·36504**	**1·07429**	**1·07392**	**1·07448**	**1·07429**
	Mean **0·36502** grm.						Mean **1·07425** grm.			

Filling of Bulb.

	grm.
Weight of bulb, etc., empty	6 ·5507
Weight of bulb, etc., filled	10 ·3829
∴ Apparent weight of water added	3 ·8322
Correction for air displaced	0 ·0038
So, real weight of water added	**3·8360**

	grm.
Mean apparent condensation with filled bulb	1 ·07425
Mean apparent condensation with emptied bulb	0 ·36502
Apparent value of difference	0 ·70923
Corrections for changes occurring inside bulb	0 ·00215
Corrections for difference of buoyancy of amounts of water condensed	0 ·00043
Whence, real difference of condensations, $m'-m$, per 100° C. temperature interval	**0·71181**
Weight of water M added to the bulb	**3·8360**

Whence, the heat of vaporisation of water boiling at 100° C. and at 1 atmosphere pressure is **538·89** mean calories.

Second Series.

—	Bulb nearly empty (three experiments).			Bulb nearly full (three experiments).		
	grm.	grm.	grm.	grm.	grm.	grm.
Weight (corrected) of bulb, etc., in air	28·00010	28·00113	28·00006	31·96441	31·96293	31·96415
Weight after chilling, etc.	28·07320	28·23117	28·31020	32·32171	31·99897	31·97324
Weight adhering mercury (recovered)	0·0583	0·2163	0·3001	0·3131	0·0114	0·0041
Weight adhering water	0·01480	0·01374	0·01004	0·04420	0·02464	0·00499
Sum of corrections for adhering mercury and adhering water	0·00310	0·00389	0·00370	0·01011	0·00469	0·00095
Weight of bulb, etc., in steam after condensation	28·52414	28·68316	28·76241	33·50840	33·18225	33·15114
∴ Apparent weight of steam condensed	0·45094	0·45199	0·45221	1·18669	1·18328	1·17790
∴ Corrected weight of steam condensed	0·44784	0·44810	0·44851	1·17658	1·17859	1·17695
	°C.	°C.	°C.	°C.	°C.	°C.
Boiling point	99·85	99·94	100·03	99·71	99·85	99·71
	grm.	grm.	grm.	grm.	grm.	grm.
Hence, apparent weight of condensation per 100° C. temperature interval	0·44851	0·44837	0·44838	1·17998	1·18036	1·18035
Correction for change in latent heat with change of temperature of boiling	0·00007	0·00003	0·00002	0·00038	0·00019	0·00038
Hence corrected apparent weight of condensation per 100° C. temperature interval	**0·44858**	**0·44840**	**0·44836**	**1·18036**	**1·18055**	**1·18073**
	Mean **0·44845** grm.			Mean **1·18055** grm.		

Filling of Bulb.

	grm.
Weight of bulb, etc., empty	6·66111
Weight of bulb, etc., filled	10·61663
∴ Apparent weight of water added	3·95552
Correction for air displaced	0·00396
So, real weight of water added	**3·95948**

	grm.
Mean apparent condensation with filled bulb	1·18055
Mean apparent condensation with emptied bulb	0·44845
Apparent value of difference	0·73210
Corrections for changes occurring within the bulb	0·00225
Correction for difference of buoyancy of amounts of water condensed	0·00044
Whence, real difference of condensations, $m'-m$, per 100° C. temperature interval	0·73479
Weight of water M added to the bulb	**3·95948**

Whence, the heat of vaporisation of water boiling at 100° C. and at 1 atmosphere pressure is **538·86** mean calories.

F. *Conclusion.*

Determination with first bulb, 538·89 mean calories.

Determination with second bulb, 538·86 mean calories.

These determinations are independent in the sense that they have been made with different bulbs and under different conditions of steam supply, and that any one measurement is used in one series only.

The values may be expected (see E) to agree to within seven or eight units in the fifth figure, a degree of accuracy that is confirmed by the experimental figures (see Tables).

The conclusion is therefore that the value

538·88 mean calories

for the heat of vaporisation of water at 100° C. and 1 atmosphere pressure is correct to the fourth significant figure for the samples of steam used; and in consideration of the results of Section E IX, it is held that the dampness of these samples has not affected the result to the extent of 1 part in 5000.

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